Variation of Film Resistance during Electropaint Deposition

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We reported the influence of glass transition temperature (T_g) of polymer resin on deposition under constant voltage condition.[1] Film deposition of a resin with high T_g shows current-time curve where current decreases abruptly. The behavior leads to deposition with high resistance. In the case of deposition from a resin with low T_g, an abrupt drop in current is not displayed and the observed current decreases monotonously. Such film behaves as the conductive. These phenomena illustrate that there are a high resistance and an ion-permeable film formation. Moreover, the images observed by atomic force microscopy (AFM) differ between both resin systems. During deposition with the high resistance, dispersed particles are piled up on the deposited particles. On the other hand, deposition of the ion-permeable film shows only a flat surface without any particles. Consequently, film structure depends obviously on the resin T_g. In the present paper, correlation between the film growth and structure is discussed from the variation of film resistance during deposition.

CALCULATION of FILM RESISTIVITY

Film resistivity

Ohmic drops for solution and film govern voltage balance during electrodeposition. According to Ohm's law, under constant voltage condition (CV), Eq. (1) is given

$$\rho_F = \frac{1}{L_F}\left(\frac{E}{i} - \rho_S L_S\right) = \frac{E}{L_F}\left(\frac{1}{i} - \frac{1}{i_0}\right) \quad (1)$$

Under constant current condition (CC), Eq. (2) is obtained

$$\rho_F = \frac{1}{L_F}\left(\frac{E}{i} - \rho_S L_S\right) = \frac{1}{iL_F}\left(E - E_0\right) \quad (2)$$

We presuppose that these equations are applied to thickness thicker than 0.5 μm.

Deposited film as a uniform resistance under CV

Providing that film resistivity keeps constant during deposition, R_F is defined as Eq. (3).

$$R_F = \rho_F \frac{Q}{\sigma A^2}\int_0^t I dt = K\int_0^t I dt \quad (3)$$

Eq. (4) is given according to Ohm's law, where K is the constant.

$$\frac{E}{I} = K\int_0^t I dt + R_S \quad (4)$$

On the basis of Eq. (4), correlation of deposition time with current is given by Eq. (5), where $k = \rho Q/\sigma E$.

$$\frac{1}{i^2} = \frac{1}{i_0^2} + kt \quad (5)$$

EXPERIMENTAL

Two cationic resins were synthesized with acrylic monomers by radical polymerization: methyl methacrylate system (MMAs, T_g = 70 ºC) and methyl acrylate system (MAs, T_g = 5 ºC). A mixture was prepared with the cationic resin and cross-linking agent. Solvents, lactic acid and deionized water were added into the mixture to prepare a bath solution of 10wt.% polymer concentration. A stainless steel plate was used as an anode. Films were deposited on a Cu-Zn alloy cathode under constant voltage (CV) or constant current (CC). Conditions for the deposition were as follows: bath temperature was 25 ºC, applied voltages varied from 2 to 150 V, current density was 0.3 to 1.0 mA/cm^2, and deposition time was 200 s. Current-time or voltage-time curves were recorded by using personal computer. Deposit weight was measured.

RESULTS and DISCUSSION

Under CV, film resistivity of the MMAs was calculated using Eq. (1). The abrupt increase in resistivity forms a peak in the resistivity-time relation. The peak height of the resistivity becomes small, as voltage is increased. Correlation of film resistivity with film thickness shows that the peak of resistivity is moved toward a position of 2 to 5 μm with an increase in voltage. In addition, the peak shape becomes broad. Under CC, MMAs film causes an abrupt rise in voltage. The period of the rise becomes brief with an increase in current density. Relation between film thickness and voltage shows that the abrupt rise takes place at thickness of 3 μm. The results are independent of current density and are determined by film thickness. Resistivity of the MMAs is calculated from Eq. (2). Change in the resistivity results in the broad peak with an increase in the film thickness. Deposited film at low current density increases the peak height of film resistivity. Film resistivity for the MMAs is 10^5 to 10^6 kΩcm under CV, and is the order of 10^5 kΩcm under CC. The deposited film under CV leads to resistivity higher than under CC. The facts are understood to be the difference in the packing densities of particles which are deposited on a substrate.

In the case of the MAs, the values of film resistivity do not differ between CV and CC, and are the order of 10^4 kΩcm. Ohmic drop of the polymer solution seems to be nearly equal to ohmic drop of the deposited film under CC and at the deposition time of 100 s. Correlation of the MAs film thickness with the resistivity shows that the resistivity of the MAs film decreases with the increase in thickness and becomes constant at thickness thicker than 6 μm. Such variation in the profile of resistivity suggests that film deposition takes place as a uniform resistance.

Eq. (5) suggests that $1/i^2$ is proportional to deposition time t if a film deposited under CV is a uniform resistance body. Deposition of the MMAs film does not follow the relation to Eq. (5). The MAs film almost satisfies the relation. Deviations from Eq. (5) show that the initial deposits for the MMAs film are porous. The MAs film deposits as a uniform resistance. The results coincide with the observation of AFM images.

In conclusions, the variation of film resistivity can presume film structure during deposition. The MMAs film leads to porous film at the early time of deposition and the prolonged time converts the deposited film to uniform resistance body. The MAs film deposits as a uniform resistance from the start of deposition.

REFFERENCES

1. Y-I. Suzuki, H. Fukui, K. Tsuchiya, S. Arita, and Y. H. Ogata, 198th ECS Fall Meeting, Abstract No. 1053, Phoenix, Arizona, 2000.

[Notation]

E: Voltage (V) E_0: Voltage at t= 0 (V) I: Total current (A) i: Current density (A/cm^2) i_o: Current density at t = 0 (A/cm2) R_F: Film resistance (Ω) R_S: Solution resistance (Ω) ρ_F: Film resistivity (Ωcm) ρ_S: Solution resistivity (Ωcm) L_F: Film thickness (cm) L_S: Electrode distance (cm) A: Surface area (cm^2) Q: Coulomb efficiency (g/C) σ_F: Film density (g/cm^3) t: Deposition time (sec)